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**APPLICATION FOR LETTERS PATENT**

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**Integrated Circuitry And Method Of Forming A  
Capacitor**

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# Integrated Circuitry And Method Of Forming A Capacitor

## TECHNICAL FIELD

This invention relates to integrated circuitry and to methods of forming capacitors.

## BACKGROUND OF THE INVENTION

As DRAMs increase in memory cell density, there is a continuing challenge to maintain sufficiently high storage capacitance despite decreasing cell area. Additionally, there is a continuing goal to further decrease cell area. One principal way of increasing cell capacitance is through cell structure techniques. Such techniques include three-dimensional cell capacitors, such as trenched or stacked capacitors. Yet as feature size continues to become smaller and smaller, development of improved materials for cell dielectrics as well as the cell structure are important. The feature size<sup>(F)</sup> of 256Mb DRAMs and beyond will be on the order of 0.25 micron or less, and conventional dielectrics such as  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  might not be suitable because of small dielectric constants. *dim*

Highly integrated memory devices, such as 256 Mbit DRAMs and beyond, are expected to require a very thin dielectric film for the 3-dimensional capacitor of cylindrically stacked or trench structures. To meet this requirement, the capacitor dielectric film thickness will be below 2.5nm of  $\text{SiO}_2$  equivalent thickness.

high K

1 Insulating inorganic metal oxide materials (such as ferroelectric materials,  
2 perovskite materials and pentoxides) are commonly referred to as "high K"  
3 materials due to their high dielectric constants, which make them attractive  
4 as dielectric materials in capacitors, for example for high density DRAMs and  
5 non-volatile memories. In the context of this document, "high K" means a  
6 material having a dielectric constant of at least 10. Such materials include  
7 tantalum pentoxide, barium strontium titanate, strontium titanate, barium titanate,  
8 lead zirconium titanate and strontium bismuth titanate. Using such materials  
9 might enable the creation of much smaller and simpler capacitor structures for  
10 a given stored charge requirement, enabling the packing density dictated by  
11 future circuit design.

12 Despite the advantages of high dielectric constants and low leakage,  
13 insulating inorganic metal oxide materials suffer from many drawbacks. For  
14 example, all of these materials incorporate oxygen or are otherwise exposed  
15 to oxygen for densification to produce the desired capacitor dielectric layer.  
16 Densification or other exposure to an oxygen containing environment is  
17 utilized to fill oxygen vacancies which develop in the material during its  
18 formation. For example when depositing barium strontium titanate, the  
19 material as-deposited can have missing oxygen atoms that may deform its  
20 crystalline structure and yield poor dielectric properties. To overcome this  
21 drawback, for example, the material is typically subjected to a high  
22 temperature anneal in the presence of an oxygen ambient. The anneal drives  
23 any carbon present out of the layer and advantageously injects additional  
24 oxygen into the layer such that the layer uniformly approaches a stoichiometry

1 of five oxygen atoms for every two tantalum atoms. The oxygen anneal is  
2 commonly conducted at a temperature of from about 400° C to  
3 about 1000° C utilizing one or more of O<sub>3</sub>, N<sub>2</sub>O and O<sub>2</sub>. The oxygen  
4 containing gas is typically flowed through a reactor at a rate of from about  
5 0.5 slm to about 10 slm.

6 Certain high K dielectric materials have better current leakage  
7 characteristics in capacitors than other high K dielectric materials. In some  
8 materials, aspects of a high K material which might be modified or tailored  
9 to achieve a highest capacitor dielectric constant are possible but will unfortunately  
10 also tend to hurt the leakage characteristics (i.e., increase current leakage).  
11 One method of decreasing leakage while maximizing capacitance is to increase  
12 the thickness of the dielectric region in the capacitor. Unfortunately, this is  
13 not always desirable.

## SUMMARY

The invention comprises integrated circuitry and methods of forming capacitors. In one implementation, integrated circuitry includes a capacitor having a first capacitor electrode, a second capacitor electrode and a high K capacitor dielectric region received therebetween. The high K capacitor dielectric region has a high K substantially amorphous material layer and a high K substantially crystalline material layer. In one implementation, a capacitor forming method includes forming a first capacitor electrode layer over a substrate. A substantially amorphous first high K capacitor dielectric material layer is deposited over the first capacitor electrode layer. The substantially amorphous high K first capacitor dielectric material layer is converted to be substantially crystalline. After the converting, a substantially amorphous second high K capacitor dielectric material layer is deposited over the substantially crystalline first high K capacitor dielectric material layer. A second capacitor electrode layer is formed over the substantially amorphous second high K capacitor dielectric material layer.

## BRIEF DESCRIPTION OF THE DRAWINGS

Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

Fig. 1 is a view of a semiconductor wafer fragment comprising integrated circuitry in accordance with an aspect of the invention.

Fig. 2 is a view of an alternate embodiment semiconductor wafer fragment comprising integrated circuitry in accordance with an aspect of the invention.

Fig. 3 is a view of a semiconductor wafer fragment in process in accordance with an aspect of the invention.

Fig. 4 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that depicted by Fig. 3.

Fig. 5 is a view of the Fig. 3 wafer fragment at a processing step subsequent to that depicted by Fig. 4.

Fig. 6 is a diagrammatic depiction of one preferred processing flow in accordance with an aspect of the invention.

Fig. 7 is a diagrammatic depiction of another preferred processing flow in accordance with an aspect of the invention.

Fig. 8 is a diagrammatic depiction of still another preferred processing flow in accordance with an aspect of the invention.

Fig. 9 is a diagrammatic depiction of example integrated circuitry in accordance with an aspect of the invention.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This disclosure of the invention is submitted in furtherance of the constitutional purposes of the U.S. Patent Laws "to promote the progress of science and useful arts" (Article 1, Section 8).

It is recognized that high K crystalline dielectric materials tend to have higher dielectric constant than high K amorphous dielectric materials. For example, amorphous Ta<sub>2</sub>O<sub>5</sub> dielectric constants range from 15 to 20, while the dielectric constants of crystalline Ta<sub>2</sub>O<sub>5</sub> can range from 35 to 45. Yet, leakage characteristics of crystalline Ta<sub>2</sub>O<sub>5</sub> are much worse than amorphous Ta<sub>2</sub>O<sub>5</sub>, and thus could potentially limit the use of crystalline Ta<sub>2</sub>O<sub>5</sub>. However, it would be desirable to take advantage of higher dielectric constants of, for example, crystalline Ta<sub>2</sub>O<sub>5</sub> as capacitor area continues to shrink.

A first embodiment example integrated circuitry in accordance with but one aspect of the invention is depicted in Fig. 1. Such comprises a semiconductor wafer fragment 10 comprising a semiconductor substrate 12 and overlying insulative layer 14, such as silicon dioxide. In the context of this document, the term "semiconductor substrate" or "semiconductive substrate" is defined to mean any construction comprising semiconductive material, including, but not limited to, bulk semiconductive materials such as a semiconductive wafer (either alone or in assemblies comprising other materials thereon), and semiconductive material layers (either alone or in assemblies comprising other materials). The term "substrate" refers to any supporting structure, including, but not limited to, the semiconductive substrates described above. Substrate region 12 in this example preferably comprises bulk monocrystalline silicon,

1 although other materials and semiconductor-on-insulator constructions are, of  
2 course, contemplated. Discussion proceeds with description of a capacitor  
3 construction 17 fabricated over substrate 12/14.

4 A first capacitor electrode layer 16 is formed over substrate 12/14.  
5 Such could comprise any suitable conductive material, with inherently  
6 conductive metals such as elemental metals and metal alloys, and conductive  
7 metal oxides, and mixtures thereof being preferred. An exemplary thickness  
8 range for electrode layer 16 is from about 100 Angstroms to about  
9 1000 Angstroms.

10 A high K capacitor dielectric region 20 is formed over first capacitor  
11 electrode layer 16. A second capacitor electrode layer 30, preferably the  
12 same as the first, is formed over high K capacitor dielectric region 20, such  
13 that high K capacitor dielectric region 20 is received between electrode  
14 layers 16 and 30. High K capacitor dielectric region 20 comprises a high K  
15 substantially crystalline material layer 22 and a high K substantially amorphous  
16 material layer 24. In the context of this document, "substantially crystalline"  
17 means greater than or equal to about 70% crystallinity, whereas "substantially  
18 amorphous" means that the subject material layer is greater than or equal to  
19 about 70% amorphous phase. More preferably the substantially crystalline and  
20 substantially amorphous materials have greater than 90%, and more preferably  
21 greater than 98% of their respective phase. A preferred thickness range for  
22 layers 22 and 24 is from about 20 Angstroms to about 250 Angstroms each.  
23 A preferred thickness range for capacitor dielectric region 20 is from about  
24 40 Angstroms to about 500 Angstroms, with such region preferably being the



1 only capacitor dielectric region which is received between first capacitor  
2 electrode 16 and second capacitor electrode 30. Accordingly preferably,  
3 high K capacitor dielectric region 20 consists essentially of high K  
4 substantially amorphous material layer 24 and high K substantially crystalline  
5 material layer 22.

6 The high K substantially amorphous material and the high K  
7 substantially crystalline material may constitute the same chemical composition,  
8 or different chemical compositions. For example, and by way of example  
9 only, layer 22 might comprise or consist essentially of barium strontium  
10 titanate, while layer 24 might comprise or consist essentially of  $Ta_2O_5$ . Most  
11 preferably, layers 22 and 24 comprise the same chemical composition, with  
12 a preferred material being  $Ta_2O_5$ , but for a phase difference in the material  
13 as described above and subsequently below. Other dielectric materials might  
14 also, of course, be received within capacitor dielectric region 20, but such is  
15 not most preferred. Further, more than the illustrated two amorphous and  
16 crystalline layers might be received there.

17 Further preferably, at least one of the high K substantially amorphous  
18 material layer and the high K substantially crystalline material layer contacts  
19 at least one of the first capacitor electrode and second capacitor electrode.  
20 Further preferably, the high K substantially amorphous material layer contacts  
21 at least one of the first capacitor electrode and the second capacitor electrode.  
22 Further preferably, the high K capacitor substantially amorphous material layer  
23 contacts only one of the first capacitor electrode and the second capacitor  
24 electrode. As shown, the high K substantially amorphous material layer

1 contacts one of the first and second capacitor electrodes (electrode 30 as  
2 shown), and the high K substantially crystalline material layer contacts the  
3 other of the first and second capacitor electrodes (electrode 16 as shown).  
4 Thus in the Fig. 1 depicted embodiment, capacitor 17 is received at least  
5 partially over semiconductor substrate 12, with the high K substantially  
6 crystalline material layer 22 being received between semiconductor substrate 12  
7 and high K substantially amorphous material layer 24.

8 Fig. 2 depicts an alternate embodiment wherein the positionings of  
9 layer 22 and 24 have been reversed. Like numerals from the first described  
10 embodiment are utilized where appropriate, with differences being indicated  
11 with the suffix "a".

12 The subject capacitors might be fabricated in any of a number of  
13 ways. Some example embodiments are described with reference to Figs. 3-8,  
14 and with reference to the Fig. 1 preferred embodiment. Like numerals from  
15 the first described embodiment are utilized where appropriate, with differences  
16 being depicted with different numerals. Referring initially to Figs. 3 and 6,  
17 a substantially amorphous first high K capacitor dielectric material layer 21  
18 is formed over first capacitor electrode layer 16, and preferably to contact  
19 electrode layer 16 as shown. Such is preferably deposited to the same  
20 thickness as layer 22 in the Fig. 1 embodiment.  $Ta_2O_5$  is the preferred  
21 material, although other substantially amorphous high K materials are of course  
22 contemplated. Any existing or yet-to-be-developed technique for forming such  
23 amorphous layer can be utilized, with no one in particular being preferred.  
24

1 Referring to Figs. 4 and 6, substantially amorphous high K first  
2 capacitor dielectric material layer 21 (not shown) is converted to be  
3 substantially crystalline, as depicted with numeral 22. A preferred technique  
4 for doing so comprises an anneal in an inert atmosphere, such as N<sub>2</sub> or Ar,  
5 at a temperature from about 650°C to about 950°C at from about 5 Torr to  
6 about 1 atmosphere from about one minute to about one hour. Accordingly  
7 preferably, the converting occurs in an atmosphere which is substantially void  
8 of oxygen.

9 Referring to Figs. 5 and 6, and after the converting, substantially  
10 amorphous second high K capacitor dielectric material layer 24 is formed over  
11 substantially crystalline first high K capacitor dielectric material layer 22.  
12 Preferably and as shown, layer 24 is formed to physically contact layer 22.

13 Then preferably, second high K capacitor dielectric material layer 24  
14 is oxidize annealed in an oxygen containing atmosphere at a temperature of  
15 no greater than about 600°C, and more preferably from about 300°C to about  
16 550°C, and effective to maintain second high K capacitor dielectric material  
17 layer 24 substantially amorphous. Preferred annealing gases include, by way  
18 of example only, N<sub>2</sub>O, O<sub>2</sub>, O<sub>3</sub>, and mixtures thereof. Preferred pressure  
19 range is from 150 mTorr to 1 atmosphere, and at a time period preferably  
20 ranging from about 10 seconds to about 1 hour. Such oxidize annealing  
21 preferably densifies and inserts oxygen in layer 24, and also into crystalline  
22 layer 22.

Purpose  
of x anneal

1 Referring to Fig. 1, second capacitor electrode layer 30 is formed over  
2 substantially amorphous second high K capacitor dielectric material layer 24,  
3 and preferably in physical contact therewith.

4 Any of a myriad of alternate processing sequences might be performed,  
5 with two such sequences being depicted in Figs. 7 and 8. Fig. 7 depicts  
6 conducting an oxidize annealing, preferably as described above, intermediate  
7 the first deposition of a substantially amorphous high K capacitor dielectric  
8 material layer and subsequent crystallization thereof. Fig. 8 depicts exemplary  
9 alternate processing whereby an oxidization anneal is conducted intermediate  
10 crystallization of the first substantially amorphous deposited high K capacitor  
11 dielectric layer and the deposit of the second substantially amorphous  
12 substantially high K dielectric layer.

13 Such integrated circuitry construction and fabrication methods might be  
14 used in a number of different applications, by way of example only in the  
15 fabrication of logic or memory circuitry, such as DRAM circuitry fabrication.  
16 Fig. 9 illustrates DRAM circuitry and fabrication thereof. A wafer  
17 fragment 110 comprises a bulk monocrystalline silicon substrate 112 having  
18 a pair of field isolation regions 114. A series of four DRAM word line  
19 constructions 116, 117, 118 and 119 are formed over the illustrated substrate,  
20 and comprise gates of respective DRAM cell field effect transistors. Gate  
21 constructions 116, 117, 118 and 119 are conventional as shown, and comprise  
22 a gate dielectric layer (not shown), an overlying conductive polysilicon region,  
23 an overlying higher conductive elemental metal or silicide region, and an  
24 insulative cap and sidewall spacers, and which are not otherwise specifically

C1

identified with numerals. In the illustrated section, word line 117 comprises a transistor access gate having associated source/drain diffusion regions 120 and 122 formed within monocrystalline silicon substrate 12. Similarly, DRAM word line 118 comprises a gate of a DRAM cell field effect transistor having an associated pair of source/drain diffusion regions 122 and 124. Such depicts two DRAM cells which share a source/drain region 22 which will electrically connect with a bit line, as described subsequently. The other respective source/drain diffusion regions 120 and (24) are formed in electrical connection with DRAM cell capacitor constructions 126 and 127, respectively. The illustrated example is in the fabrication of bit line-over-capacitor DRAM integrated circuitry construction, although other DRAM integrated circuitry and other integrated circuitry constructions and fabrication methods are contemplated.

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Conductive covering regions 134 are formed over source/drain regions 120, 122 and 124. Such might be formed to have outermost surfaces or tops which are received elevationally below the outermost top surfaces of gate constructions 116-119 as shown, or received elevationally thereabove (not shown). Such might comprise conductive polysilicon, metals, and/or metal compounds, including conductive barrier layer materials.

An insulating layer 128, for example borophosphosilicate glass (BPSG), is formed over the word lines and is planarized as shown. An antireflective coating layer or layers (not shown) might preferably comprise an outermost portion of layer 128, and comprise silicon oxynitride which can also function as a diffusion barrier to hydrogen and other gases. Capacitor container

1 openings 130 and 131 are formed within insulative layer 128 over source/drain  
2 diffusion regions 120 and 124, respectively, and the associated conductive  
3 covering regions 134. A capacitor storage node layer 136 is formed within  
4 container openings 130 and 131 in electrical connection with source/drain  
5 diffusion regions 120 and 124 through conductive covering/plugging  
6 material 134. Such can be planarized back to be isolated within the  
7 container openings as shown. Example materials include conductively doped  
8 polysilicon, metal and metal compounds, with conductive metal oxides being  
9 preferred materials. Example conductive metal oxides include ruthenium oxide,  
10 iridium oxide, and rhodium oxide.

11 A capacitor dielectric layer 138 is formed over storage node electrode  
12 layer 136. Layer 138 preferably is fabricated to comprise any of the above  
13 capacitor dielectric regions 20, 20a or others as described above. A DRAM  
14 capacitor cell electrode layer 140 is formed over capacitor dielectric layer 138.  
15 Cell electrode layer 140 is preferably common to multiple capacitors of the  
16 DRAM circuitry, and preferably comprises a conductive metal oxide.  
17 Layer 140 is patterned as desired and shown to provide an opening  
18 therethrough to ultimately achieve bit line electrical connection with shared  
19 diffusion region 122 (shown and described below), and to otherwise form a  
20 desired circuitry pattern thereof outwardly of the fragment depiction of Fig. 9.

21 An insulative layer 144 is formed over DRAM capacitor cell electrode  
22 layer 140. An example and preferred material is BPSG. A contact  
23 opening is formed through insulative layers 144 and 128 for ultimate  
24 formation of a conductive bit contact. Conductive material 156 is formed

C2

1 within the contact opening in electrical connection with DRAM capacitor cell  
2 electrode layer 140 and within contact opening 146 in electrical connection  
3 with bit contact source/drain diffusion region 122. Conductive material 156  
4 preferably comprises a metal and/or metal compound which is/are capable of  
5 oxidizing to a non-conductive metal oxide upon effective exposure to the  
6 conductive metal oxide of layer 140. Preferred materials include titanium,  
7 titanium nitride, and tungsten, by way of example only. Such layers are  
8 deposited and planarized back relative to insulative layer 144 as shown.

9 A conductive layer 165 is deposited over and in electrical connection  
10 with conductive material 156. Such is patterned to form a DRAM bit  
11 line 166 over insulative layer 144 and in electrical connection with  
12 source/drain diffusion region 122 through conductive material 156. Other  
13 devices might be formed outwardly of layer 168, followed ultimately by  
14 formation of a final passivation layer.

15 In compliance with the statute, the invention has been described in  
16 language more or less specific as to structural and methodical features. It  
17 is to be understood, however, that the invention is not limited to the specific  
18 features shown and described, since the means herein disclosed comprise  
19 preferred forms of putting the invention into effect. The invention is,  
20 therefore, claimed in any of its forms or modifications within the proper  
21 scope of the appended claims appropriately interpreted in accordance with the  
22 doctrine of equivalents.

23  
24

Phot shown  
in Fig 9